

(12) **Patent Application Publication** (10) **Pub. No.: US 2019/0352784 A1**
Schouten et al. (43) **Pub. Date: Nov. 21, 2019**

Nov. 24, 2016 (NL) 2017869

Publication Classification

(51) **Int. Cl.**
C25B 3/02 (2006.01)
C25B 3/04 (2006.01)
C07D 307/68 (2006.01)

(52) **U.S. CI.**
CPC **C25B 3/02** (2013.01); **C25B 9/08**
(2013.01); **C07D 307/68** (2013.01); **C25B 3/04**
(2013.01)

(57) **ABSTRACT**

A process for treating a furan-2,5-dicarboxylic acid composition, which process comprises: introducing a furan-2,5-dicarboxylic acid composition, which furan-2,5-dicarboxylic acid composition contains an impurity compound and which impurity compound is 5-formyl-furan-2-carboxylic acid, into a cathode compartment of an electrochemical cell; and electrochemically reducing the impurity compound in the cathode compartment.

§ 371 (c)(1),

(2) Date: **May 17, 2019**

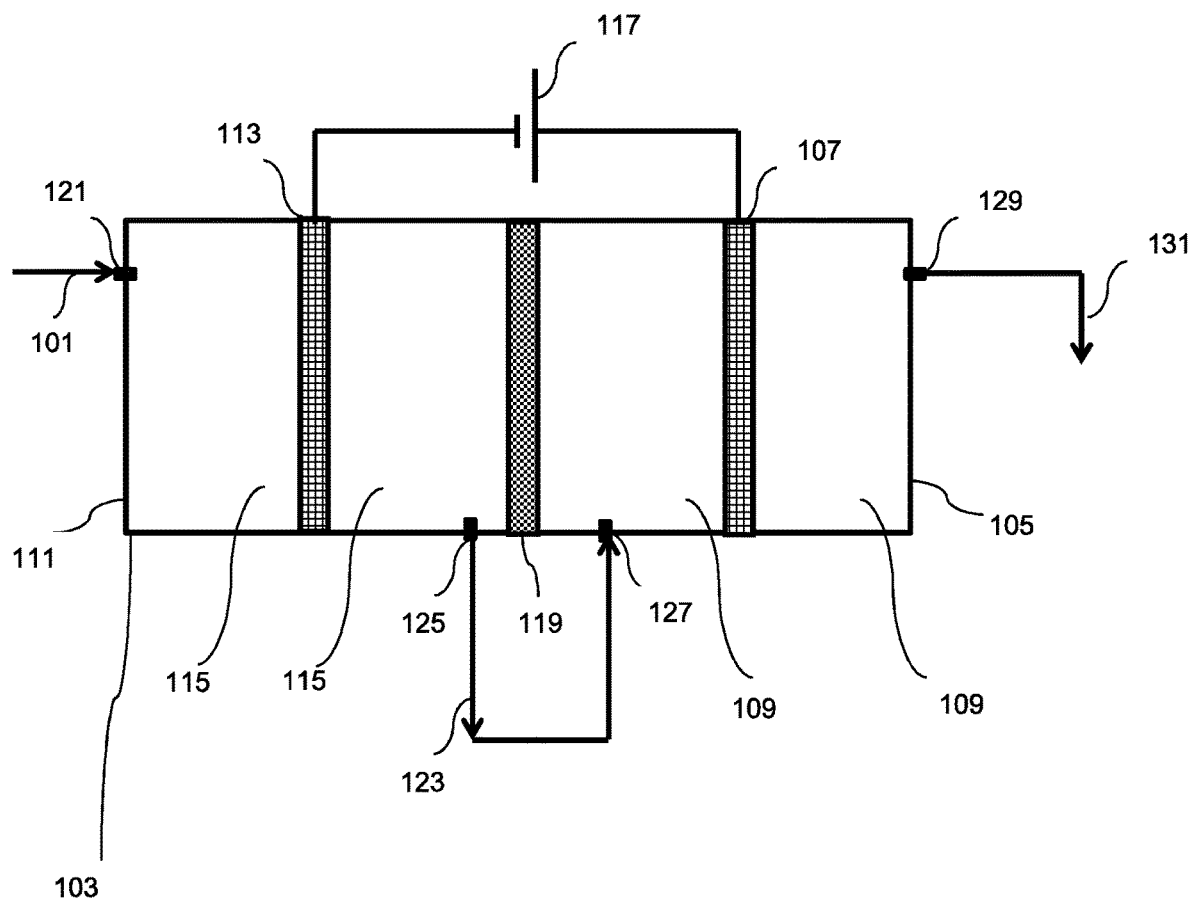
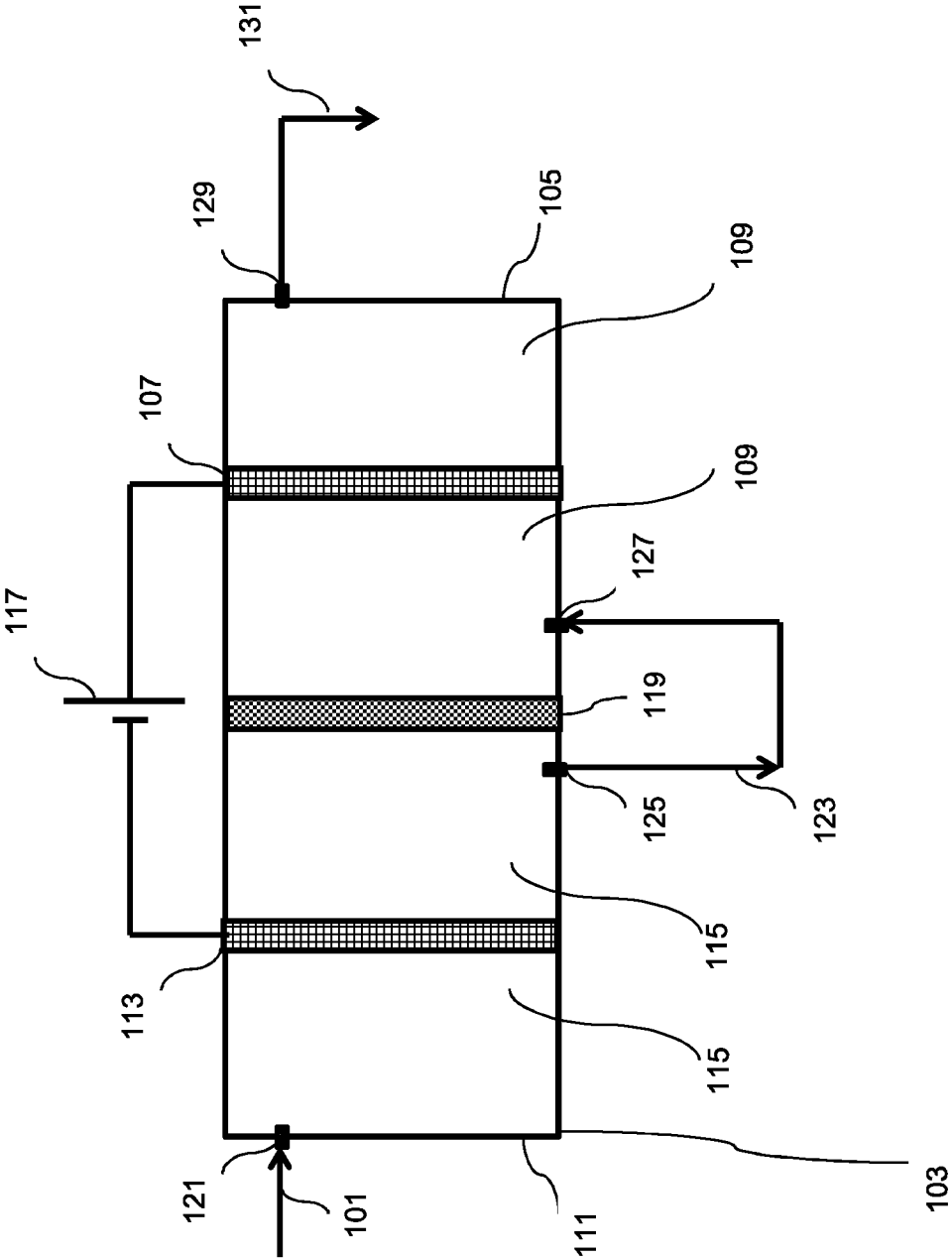


Figure 1



PROCESS FOR TREATING A FURAN-2,5-DICARBOXYLIC ACID COMPOSITION

FIELD OF THE INVENTION

[0001] The invention relates to a process for treating a furan-2,5-dicarboxylic acid composition.

BACKGROUND TO THE INVENTION

[0002] Dicarboxylic acids are widely used in the chemical industry as a starting material for the production of polymers.

[0003] An example is furan-2,5-dicarboxylic acid (FDCA) which can be polymerized in the presence of ethylene glycol (EG) to form poly ethylene furanoate (PEF).

[0004] The chemical preparation of polymer grade dicarboxylic acids, such as for example polymer grade furan-2,5-dicarboxylic acid, from relatively less pure or "crude" dicarboxylic acid is cumbersome.

[0005] In US 2013/0345452 it is explained that FDCA can be synthesized by the catalytic oxidation of 5-(hydroxymethyl)furfural (HMF); or by the catalytic oxidation of HMF esters (5-R(CO)OCH₂-furfural where R=alkyl, cycloalkyl and aryl); or by the catalytic oxidation of HMF ethers (5-R'OCH₂-furfural, where R'=alkyl, cycloalkyl and aryl); or by the catalytic oxidation of 5-alkyl furfurals (5-R"-furfural, where R"=alkyl, cycloalkyl and aryl) whilst using a Co/Mn/Br catalyst system. Mixed feedstocks of HMF and HMF esters, mixed feedstocks of HMF and HMF ethers, and mixed feedstocks of HMF and 5-alkyl furfurals can also be used. US 2013/0345452 further describes a process for purifying a crude FDCA composition by hydrogenation in the presence of a hydrogenation catalyst in a hydrogenation solvent such as water at a temperature within a range of 130° C. to 225° C. The hydrogenation needs to be conducted at a temperature where FDCA is sufficiently soluble in water. Unfortunately in the process of US 2013/0345452 not only 2-formyl-furan-5-carboxylic acid is hydrogenated, but also 2,5-furandicarboxylic acid appears to be partly hydrogenated into tetrahydrofuran-2,5-dicarboxylic Acid (THFDCA)

[0006] WO 2015/030590 explains that the purification of 2,5-furandicarboxylic acid containing compositions that also contain 2-formyl-furan-5-carboxylic acid are difficult to purify by recrystallization. WO 2015/030590 therefore proposes a process for purifying an acid composition comprising 2-formyl-furan-5-carboxylic acid and 2,5-furandicarboxylic acid, which process comprises an esterification to obtain an esterified composition and subsequent separation of the ester from the esterified composition. It is, however, evident that this proposed method remains cumbersome.

[0007] It would be an advancement in the art to provide a process for the treatment of a furan-2,5-dicarboxylic acid composition which is less cumbersome.

[0008] Non-pre published patent application WO2016/186504 describes a process wherein a feedstock comprising at least an aromatic aldehyde compound is introduced into an electrolytic cell comprising electrodes, wherein at least one of the electrodes comprises a non-noble metal and/or an oxide and/or a hydroxide thereof and/or carbon; and wherein the aromatic aldehyde compound is electrochemically oxidized to yield an aromatic dicarboxylic acid. According to examples 2 and 3 of WO2016/186504, the resulting products

contained less color bodies. Non-pre published patent application WO2016/186505 describes a process for the purification of a carboxylic acid-containing composition, which composition further contains an aldehyde, which process comprises electrochemically oxidizing the aldehyde in an electrolytic cell to obtain an electrochemically oxidized product composition comprising a carboxylic acid derived from the aldehyde and optionally separating carboxylic acid from the electrochemically oxidized product composition.

[0009] Although good results are obtained with the processes of WO2016/186504 and WO2016/186505, there is still room for alternative processes and further improvement.

[0010] It would therefore be an advancement in the art to have a process with which similar, better, or economically more advantageous results can be achieved.

SUMMARY OF THE INVENTION

[0011] Such a process has been achieved with the process according to the invention. Accordingly the present invention provides a process for treating a furan-2,5-dicarboxylic acid composition, which process comprises:

[0012] introducing a furan-2,5-dicarboxylic acid composition, which furan-2,5-dicarboxylic acid composition contains an impurity compound and which impurity compound is 5-formyl-furan-2-carboxylic acid, into a cathode compartment of an electrochemical cell; and

[0013] electrochemically reducing the impurity compound in the cathode compartment.

[0014] By electrochemically reducing the impurity compound, i.e. the 5-formyl-furan-2-carboxylic acid, the process is suitably producing one or more impurity reduction products, i.e. one or more of reduction products of 5-formyl-furan-2-carboxylic acid.

[0015] The process according to the invention conveniently allows one to selectively reduce carbonyl groups, such as the aldehyde group in 5-formyl-furan-2-carboxylic acid.

[0016] Conveniently such carbonyl groups can be selectively reduced, whilst carboxyl groups, such as the carboxyl groups of the furan-2,5-dicarboxylic acid, are essentially maintained intact.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] FIG. 1 shows a schematic diagram of a first process according to the invention.

DETAILED DESCRIPTION OF THE INVENTION

[0018] The furan-2,5-dicarboxylic acid composition used in the process according to the invention can conveniently be a composition containing the furan-2,5-dicarboxylic acid, 5-formyl-furan-2-carboxylic acid, and optionally one or more additional impurity compounds. By an impurity compound is herein understood an organic compound other than the furan-2,5-dicarboxylic acid. As explained in more detail below, such impurity compounds may include colored compounds, and as a result of their presence the furan-2,5-dicarboxylic acid composition may have a distinguished color.

[0019] Preferably the one or more additional impurity compounds contain or consist of an organic compound comprising a carbonyl group. The process according to the invention is especially advantageous where the furan-2,5-

dicarboxylic acid composition contains a, preferably aromatic, organic compound comprising a carbonyl group. The process according to the invention allows one to selectively reduce such carbonyl group(s). Conveniently the carbonyl group may be selectively reduced, whilst the carboxyl groups are essentially maintained intact. Such organic compound comprising the carbonyl group can suitably be an aldehyde or a ketone. For example, the organic compound comprising the carbonyl group can be a dimer or polymer where the monomers are coupled via a carbonyl group. Preferably such an organic compound comprising the carbonyl group is an aromatic compound comprising a carbonyl group, more preferably the organic compound comprising the carbonyl group is an aromatic compound comprising both a carbonyl group and a carboxyl group.

[0020] Preferably the furan-2,5-dicarboxylic acid composition contains or consists of furan-2,5-dicarboxylic acid and 5-formyl-furan-2-carboxylic acid, and optionally a solvent.

[0021] The furan-2,5-dicarboxylic acid composition can suitably contain in the range from equal to or more than 1 parts per billion by weight (ppbw), more preferably equal to or more than 1 parts per million by weight (ppmw), to equal to or less than 50 wt %, more preferably equal to or less than 10 wt % of impurity compounds, based on the total weight of organic compounds in the furan-2,5-dicarboxylic acid composition. More suitably the furan-2,5-dicarboxylic acid composition can contain in the range from equal to or more than 10 ppmw to equal to or less than 1 wt % of impurity compounds, based on the total weight of organic compounds in the furan-2,5-dicarboxylic acid composition. The remaining part of the organic compounds in the furan-2,5-dicarboxylic acid composition is preferably made up of the furan-2,5-dicarboxylic acid itself.

[0022] More suitably, the furan-2,5-dicarboxylic acid composition can contain in the range from equal to or more than 1 parts per billion by weight (ppbw), more preferably equal to or more than 1 parts per million (ppmw), to equal to or less than 50 wt %, more preferably equal to or less than 10 wt % of 5-formyl-furan-2-carboxylic acid, based on the total weight of organic compounds in the furan-2,5-dicarboxylic acid composition. More suitably the furan-2,5-dicarboxylic acid composition can contain in the range from equal to or more than 10 ppmw to equal to or less than 1 wt % of 5-formyl-furan-2-carboxylic acid, based on the total weight of organic compounds in the furan-2,5-dicarboxylic acid composition. The remaining part of the organic compounds in the furan-2,5-dicarboxylic acid composition is preferably made up of the furan-2,5-dicarboxylic acid itself.

[0023] In addition to the furan-2,5-dicarboxylic acid and impurity compounds, such as for example the 5-formyl-furan-2-carboxylic acid, the furan-2,5-dicarboxylic acid composition can contain other non-organic compounds. For example in addition to the dicarboxylic acid and impurity compounds, such as for example the aldehyde as described above, the furan-2,5-dicarboxylic acid composition can contain an electrolyte solution as described below.

[0024] Aromatic dicarboxylic acids, such as furan-2,5-dicarboxylic acid, are obtainable by or can suitably be obtained, directly or indirectly, by oxidation of the corresponding dialkyl aromatic compounds.

[0025] Furan-2,5-dicarboxylic acid can conveniently be produced by means of a process comprising oxidation of

5-hydroxymethylfurfural or ethers and/or esters thereof. Suitable processes have been described in U.S. Pat. Nos. 8,865,921 and 8,519,167.

[0026] The process according to the invention can be especially advantageous where the furan-2,5-dicarboxylic acid composition used as a feed has a significant color. As mentioned above the furan-2,5-dicarboxylic acid composition may include one or more colored compounds, and as a result of their presence the furan-2,5-dicarboxylic acid composition may have a distinguished color. The color level of the furan-2,5-dicarboxylic acid composition can be ascertained visually and/or any change of color can conveniently be measured by the so-called b^* -value on the Hunter Color Scale as described in Hunter, "The measurement of Appearance", Chapter 8, pages 102-132, as published by John Wiley & Sons, NY, NY (1975) and in Wyszecki et al. "Color Science, Concepts and Methods, Quantitative Data and Formulae", 2nd Ed., pages 166-168, John Wiley & Sons, NY, NY (1982). The b^* -value of terephthalic acid can further be determined using, for example a Spectrophotometer as described for example in U.S. Pat. No. 4,626,598 and as incorporated herein by reference.

[0027] Without wishing to be bound by any kind of theory, it is believed that by means of reduction in the cathode compartment of an electrochemical cell also some colorants can potentially be removed.

[0028] Preferably, the furan-2,5-dicarboxylic acid composition in the process according to the invention is partly or wholly obtained by means electrochemically oxidizing a feedstock containing a furan-2,5-dicarboxylic acid precursor.

[0029] In a preferred embodiment, the process according to the invention is a process for producing and treating a furan-2,5-dicarboxylic acid composition, wherein the process comprises:

[0030] introducing a feedstock containing a furan-2,5-dicarboxylic acid precursor into an anode compartment of an electrochemical cell;

[0031] electrochemically oxidizing the furan-2,5-dicarboxylic acid precursor in the anode compartment, thereby producing a furan-2,5-dicarboxylic acid composition containing an impurity compound;

[0032] introducing the furan-2,5-dicarboxylic acid composition containing the impurity compound, into a cathode compartment of an electrochemical cell; and

[0033] electrochemically reducing the impurity compound in the cathode compartment,

As indicated above, the impurity compound is suitably 5-formyl-furan-2-carboxylic acid. By electrochemically reducing the impurity compound, i.e. the 5-formyl-furan-2-carboxylic acid, the process is suitably producing one or more impurity reduction products, i.e. one or more of reduction products of 5-formyl-furan-2-carboxylic acid.

[0034] More preferably the feedstock is a feedstock containing a furan-2,5-dicarboxylic acid and a furan-2,5-dicarboxylic acid precursor. Preferably such a feedstock containing a furan-2,5-dicarboxylic acid and a furan-2,5-dicarboxylic acid precursor is the product of an oxidation process as described above. Hence, preferably the feedstock is a feedstock containing furan-2,5-dicarboxylic acid and a furan-2,5-dicarboxylic acid precursor, which is preferably obtained or obtainable by oxidation of a corresponding dialkyl aromatic compound.

Preferably the furan-2,5-dicarboxylic acid precursor is 5-hydroxymethylfurfural, an ether and/or an ester thereof, or a mixture of such.

[0035] In such a process it may be advantageous to change the pH in between steps. That is, it may be advantageous to carry out the oxidation of the furan-2,5-dicarboxylic acid precursor at a pH of equal to or more than 10, whilst carrying out the reduction of the one or more impurity compounds, such as 5-formyl-furan-2-carboxylic acid, at a pH of equal to or less than 4.

[0036] Without wishing to be bound by any kind of theory it is believed that the oxidation of a corresponding dialkyl aromatic compound as described in the prior art results in a crude furan-2,5-dicarboxylic acid composition, which crude furan-2,5-dicarboxylic acid composition contains the intended furan-2,5-dicarboxylic acid and intermediate products, such as for example a formyl-substituted furan carboxylic acid (e.g. 5-formyl-furan-2-carboxylic acid) or a hydroxymethyl-substituted furan carboxylic acid (e.g. 5-hydroxymethyl-furan-2-carboxylic acid). Such intermediate products, for example a 5-formyl-furan-2-carboxylic acid or a 5-hydroxymethyl-furan-2-carboxylic acid, can be suitable furan-2,5-dicarboxylic acid precursors in the feedstock to the above mentioned anode compartment and can suitably be electrochemically oxidized into the furan-2,5-dicarboxylic acid. Any intermediate products, such as 5-formyl-furan-2-carboxylic acid, that are not fully oxidized in such anode compartment remain present in the produced furan-2,5-dicarboxylic acid composition as an impurity compound.

[0037] In the process according to the invention, the furan-2,5-dicarboxylic acid composition is introduced into a cathode compartment of an electrochemical cell. By a cathode compartment of an electrochemical cell is herein understood a compartment of an electrochemical cell containing a cathode, wherein suitably such cathode is a working electrode. By a working electrode is herein preferably understood an electrode in an electrochemical system at which a reaction of interest is occurring. In addition to the cathode the cathode compartment suitably contains a cathodic electrolyte solution. By a cathodic electrolyte solution is herein suitably understood an electrolyte solution present in the cathode compartment, which solution is in contact with the cathode.

[0038] By an anode compartment is herein understood a compartment of an electrochemical cell containing an anode, wherein suitably such anode is a working electrode. In addition to the anode the anode compartment suitably contains an anodic electrolyte solution. By an anodic electrolyte solution is herein suitably understood an electrolyte solution present in the anode compartment, which solution is in contact with the anode.

[0039] In the process according to the invention the cathode compartment and an optional anode compartment can suitably be part of the same divided electrochemical cell or the cathode compartment can suitably be part of a first, divided or undivided, electrochemical cell and the optional anode compartment can suitably be part of a second, divided or undivided, electrochemical cell.

[0040] If the electrochemical cell is an undivided electrochemical cell, the cathode, as a working electrode, is suitably accompanied by an anode, as a counter electrode. That is, the undivided electrochemical cell will contain both a cathode as well as an anode in the cathode compartment.

[0041] In a preferred embodiment the process according to the invention is a process comprising:

[0042] introducing a furan-2,5-dicarboxylic acid composition, which furan-2,5-dicarboxylic acid composition contains an impurity compound, into an undivided electrochemical cell, which undivided electrochemical cell contains a cathode and an anode; and

[0043] electrochemically reducing the impurity compound at the cathode.

As indicated above, the impurity compound is suitably 5-formyl-furan-2-carboxylic acid. By electrochemically reducing the impurity compound, i.e. the 5-formyl-furan-2-carboxylic acid, the process is suitably producing one or more impurity reduction products, i.e. one or more of reduction products of 5-formyl-furan-2-carboxylic acid.

[0044] In such a process the undivided electrochemical cell preferably further comprises an electrolyte solution having a pH of equal to or less than 4, or a pH of equal to or more than 10.

[0045] Other preferences are as outlined above.

[0046] If the electrochemical cell is a divided electrochemical cell, the cathode, as a working electrode, is suitably located in a cathode compartment whilst the anode, whether as counter electrode or as working electrode, is suitably located in another compartment.

[0047] In a preferred embodiment the process according to the invention is a process comprising:

[0048] introducing a furan-2,5-dicarboxylic acid composition, which furan-2,5-dicarboxylic acid composition contains an impurity compound, into a divided electrochemical cell, which divided electrochemical cell contains a cathode in a cathode compartment and an anode in a separate other compartment; and

[0049] electrochemically reducing the impurity compound at the cathode.

As indicated above, the impurity compound is suitably 5-formyl-furan-2-carboxylic acid. By electrochemically reducing the impurity compound, i.e. the 5-formyl-furan-2-carboxylic acid, the process is suitably producing one or more impurity reduction products, i.e. one or more of reduction products of 5-formyl-furan-2-carboxylic acid.

[0050] In such a process the divided electrochemical cell preferably further comprises an electrolyte solution in the cathode compartment having a pH of equal to or less than 4 or equal to or more than 10, more preferably equal to or more than 13.

[0051] Preferably any electrochemical cell in the process according to the invention is a divided electrochemical cell, which divided electrochemical cell includes at least a cathode compartment and an anode compartment, wherein the cathode compartment contains a cathode and a cathodic electrolyte solution and the anode compartment contains an anode and an anodic electrolyte solution. The anode and cathode of such a divided electrochemical cell are suitably connected to a power supply, capable of applying a potential over the anode and cathode. The electrochemical cell may or may not further be provided with a reference electrode. If present, the reference electrode may be a standard hydrogen electrode. Such a standard hydrogen electrode may provide an indication for the potential to cause the reduction reaction. Preferably, however, the electrochemical cell is operated in the absence of a reference electrode.

[0052] The cathode compartment and the anode compartment in such a divided electrochemical cell are conveniently

separated from each other, for example by a semi-porous membrane, made from e.g. sintered glass, porous porcelain, polytetrafluoro ethylene (PTFE or Teflon®) or polyolefin such as polyethylene or polypropylene. The electrolyte solution in the cathode compartment, i.e. the cathodic electrolyte solution, and the electrolyte solution in the anode compartment, i.e. the anodic electrolyte solution, can be the same or different.

[0053] The cathode and the anode may each be made of a variety of materials. The material of the cathode and the anode may for example each independently be chosen from the group consisting of gold, silver, nickel, palladium, platinum, chromium, ruthenium, rhodium, osmium, iridium, indium, bismuth, copper, tin, iron, lead and compounds or alloys thereof and/or hydroxides and/or oxides thereof. Also carbon can also be used as the material of either or both the cathode and/or the anode, for example the cathode and/or the anode may contain or comprise graphite.

[0054] The cathode and/or anode, herein also referred to as electrodes, may suitably comprise noble metal with the oxide and/or hydroxide thereof. Such an electrode may be similar to the one used in the article by Grabowski et al. (*Electrochimica Acta*, 36 (1991) 1995). It has been found that the use of nickel or copper as material for the cathode and/or anode is advantageous.

[0055] The cathode and/or anode material can be present as a rod, plate, mesh, foam, cloth, or in the form of small particles deposited on a carrier, such as a carbon carrier. Preferably the cathode contains or consists of copper, nickel, carbon, indium or bismuth, most preferably the cathode contains or consists of copper. Most preferably the cathode contains or consists of a copper or nickel mesh or a carbon cloth.

[0056] The electrolyte solution(s) can vary widely and can be any electrolyte solution known by the person skilled in the art to be suitable for an electrochemical reaction as set out in the currently claimed process. Preferably the electrolyte solution is an aqueous electrolyte solution. The electrolyte solution may, however, advantageously also contain or consist of acetic acid or methanol. Acetic acid and methanol are often used as solvent in a process comprising the oxidation of the corresponding dialkyl aromatic compounds, directly or indirectly resulting in the furan-2,5-dicarboxylic acid composition as explained herein above. The process according to the present invention advantageously allows one to avoid any crystallization or recrystallization steps and advantageously allows one to use the furan-2,5-dicarboxylic acid containing product of a process wherein a dialkyl aromatic compound is oxidized in the presence of an acetic acid or methanol solvent directly as feedstock in a process of the current invention.

[0057] The cathodic electrolyte solution in the cathode compartment containing the cathode preferably has a pH of equal to or below 4.0 or equal to or above 10.0. If the electrolyte solution is an aqueous electrolyte solution having a pH of equal to or more than 10.0, such electrolyte solution may also be referred to herein as an alkaline electrolyte solution. The alkalinity can facilitate the dissolution of the furan-2,5-dicarboxylic acid. Suitably, such an alkaline electrolyte solution can comprise an alkaline compound selected from an alkali metal hydroxide, alkali metal carbonate, alkali metal bicarbonate, ammonia, ammonium carbonate, ammonium bicarbonate, a trialkylamine and combinations thereof. The use of weak acids and bases, such as carbonate

and bicarbonate, has the advantage that they provide a buffering effect. The trialkylamine can suitably contain alkyl groups with 1 to 4 carbon atoms, preferably 1 or 2 carbon atoms. Suitable amines include trimethyl amine and triethyl amine. The aqueous electrolyte may comprise such an amount of an alkaline compound that the aqueous electrolyte, in spite of the presence of the furan-2,5-dicarboxylic acid, is still alkaline. The pH of the aqueous electrolyte is then suitably in the range of 10.0 to 14.0.

[0058] If the electrolyte solution is an aqueous electrolyte solution having a pH of equal to or below 4.0, such electrolyte solution may also be referred to herein as an acidic electrolyte solution. The electrolyte solution may suitably be formed by the combination of water and furan-2,5-dicarboxylic acid composition, and the ions are provided by the carboxyl function in the furan-2,5-dicarboxylic acid and optionally one or more impurity compounds, when such impurity compound(s) also comprises a carboxyl group, such as 5-formyl-furan-2-carboxylic acid. Suitably the cathodic electrolyte solution may be an acetic aqueous electrolyte solution, suitably having a PH value of 0.5 to 4.0.

[0059] As already indicated above, the electrolyte solution does not need to consist of water and ions only. The electrolyte may conveniently also comprise one or more organic diluents. Suitable diluents include water-miscible organic compounds, such as alcohols, acids, aldehydes, ketones or sulfoxides. Examples of suitable diluents include methanol, ethanol, n-propanol, i-propanol, n-butanol, i-butanol and t-butanol, formaldehyde, acetone, acetic acid and dimethylsulfoxide. The electrolyte solution may further conveniently contain electrolytes derived from compounds such as sulfuric acid, perchloric acid and salts. A wide variety of electrolytes can be used, including for example sodium (Na⁺), chloride (Cl⁻), bromide (Br⁻), potassium (K⁺), magnesium (Mg⁺⁺), zinc (Zn⁺⁺), calcium (Ca⁺⁺), phosphate (HPO₄⁻) and bicarbonate (HCO₃⁻).

[0060] The electrolyte solution(s) preferably contain water at least in an amount of 5% wt, based on the total weight of the electrolyte solution, more preferably at least 50% wt, and most preferably at least 90% wt, based on the total weight of the electrolyte solution. The temperature applied during the electrochemical reduction and/or electrochemical oxidation may vary widely. Suitably a temperature is applied where furan-2,5-dicarboxylic acid is sufficiently soluble in water. Preferably the temperature applied during the electrochemical reduction and/or electrochemical oxidation ranges from equal to or more than 0° C. to equal to or less than 250° C., more preferably from equal to or more than 135° C. to equal to or less than 200° C.

[0061] In the process according to the invention, an electrical potential is applied to the anode respectively the cathode. If the electrochemical cell in the process according to the invention is a divided electrochemical cell, and the above-mentioned cathode compartment and the above-mentioned anode compartment are present in the same divided electrochemical cell, the electrical potential is suitably applied between such anode and cathode of such divided electrochemical cell. If the above-mentioned cathode compartment is present in a first electrochemical cell and the above-mentioned anode compartment is present in a second, separate electrochemical cell, the electrochemical potential is suitably applied between the cathode, as working electrode, and a different anode, as counter electrode in the first electrochemical cell and between the anode, as working

electrode, and a different cathode, as counter electrode, in the second electrochemical cell.

[0062] As illustrated in the examples, the process can suitably comprise reducing an organic compound comprising a carbonyl group, such as the 5-formyl-furan-2-carboxylic acid, thereby producing one or more reduction products. Without wishing to be bound by any kind of theory it is believed that optionally a product composition can be obtained containing the, suitably colorless, furan-2,5-dicarboxylic acid and one or more colorless reduction products.

[0063] The conditions in the electrochemical cell can vary widely, but one skilled in the art can easily determine the potential and current in the electrochemical cell of a sufficient magnitude to produce the chemical reactions desired. The potential difference between anode and cathode in the electrochemical cell or electrochemical cells, as applicable, is suitably below 10 V, more preferably below 1.23 V. By applying a voltage below 1.23 V the electrolysis of water is avoided. The desired voltage can be provided by installing a predetermined current or current density. The current may vary within wide limits as determined by the shape, size and other parameters of the electrochemical cell. Preferably the current density is varied between 0.1 mA/cm² and 10 A/cm², more preferably from 0.2 mA/cm² to 1 A/cm². The total current is adapted according to the surface of the smallest electrode. The reaction is typically prolonged at these conditions until the desired reactions take place.

[0064] The use of a divided electrochemical cell advantageously allows one to carry out one conversion in the cathode compartment and another conversion in the anode compartment.

[0065] The process according to the invention can conveniently be combined with the processes as described in WO2016/186504 and/or WO2016/186505. The processes as described in WO2016/186504 and/or WO2016/186505 can advantageously be carried out in the anode compartment of a divided electrochemical cell, or a second, separate electrochemical cell, whilst carrying out the process according to the current invention in the cathode compartment of the divided electrochemical cell, respectively a first electrochemical cell. As explained above, this conveniently allows one to prepare a, preferably purified, furan-2,5-dicarboxylic acid composition in the anode compartment of the divided electrochemical cell, whereafter the furan-2,5-dicarboxylic acid composition prepared in such anode compartment can advantageously be introduced in the cathode compartment of another or the same divided electrochemical cell to further purify, and optionally decolorize, such furan-2,5-dicarboxylic acid composition.

[0066] Preferably, the furan-2,5-dicarboxylic acid composition that is introduced in the cathode compartment of a divided electrochemical cell, contains a dicarboxylic acid which has at least partly been obtained by oxidizing a feedstock containing one or more furan-2,5-dicarboxylic acid precursors in the anode compartment of such same divided electrochemical cell. Preferably such feedstock containing one or more furan-2,5-dicarboxylic acid precursors includes the corresponding alkanol, aldehyde or any mixture thereof of the furan-2,5-dicarboxylic acid.

[0067] The present invention therefore also provides a process comprising treating a feedstock comprising a furan-2,5-dicarboxylic acid and one or more furan-2,5-dicarboxylic acid precursors in a divided electrochemical cell, which divided electrochemical cell comprises a cathode compart-

ment containing a cathode and a cathodic electrolyte solution and an anode compartment containing an anode and an anodic electrolyte solution, which process comprises:

i) introducing the feedstock into the anode compartment of the divided electrochemical cell; and electrochemically oxidizing the furan-2,5-dicarboxylic acid precursor at the anode to thereby produce a furan-2,5-dicarboxylic acid composition, which furan-2,5-dicarboxylic acid composition contains one or more impurity compounds; and

ii) introducing the furan-2,5-dicarboxylic acid composition into the cathode compartment of the divided electrochemical cell, and electrochemically reducing at least part of the one or more impurity compounds.

[0068] As explained above, the one or more impurity compounds may include colored compounds, and as a result of their presence the furan-2,5-dicarboxylic acid composition may have a distinguished color. Preferences for the impurity compounds and furan-2,5-dicarboxylic acid composition are as described above. The feedstock used in the process comprising steps i) and ii) above preferably comprises a furan-2,5-dicarboxylic acid obtained by oxidation of a dialkyl aromatic compound as described herein before. Preferences for the anode material and cathode material are also as described above. The pH of the anodic electrolyte solution, present in the anode compartment, may vary widely but preferably the anodic electrolyte solution has a pH of equal to or less than 4.0. Preferences for the anodic electrolyte solution in respect of the electrolyte are as described above for the cathodic electrolyte solution. The oxidation in step i) and the reduction in step ii) are suitably achieved by applying an electrical potential between the anode and the cathode of the electrochemical cell. Preferences for the potential and current are as described above.

[0069] The process according to the invention and the process comprising steps i) and ii) described above can suitably be carried out batch-wise, semi batch-wise or continuously. When carried out continuously the reduction in the cathode compartment of the divided electrochemical cell and the oxidation in the anode compartment of the divided electrochemical cell are conveniently carried out simultaneously.

[0070] The impurity reduction products, such as the one or more reduction products of 5-formyl-furan-2-carboxylic acid, mentioned for the above processes may suitably comprise one or more organic compounds comprising a hydroxyl group. More suitably the impurity reduction products mentioned for the above processes may include one or more alcohols, such as for example 5-hydroxymethyl-furan-2-carboxylic acid (HMFA), which is a reduction product of 5-formyl-furan-2-carboxylic acid.

[0071] Conveniently an electrochemically reduced product composition is obtained, comprising furan-2,5-dicarboxylic acid and such 5-hydroxymethyl-furan-2-carboxylic acid. More preferably such an electrochemically reduced product composition is containing furan-2,5-dicarboxylic acid and in the range from equal to or more 1 ppbw, more preferably equal to or more than 10 ppmw to equal to or less than 1 wt % of 5-hydroxymethyl-furan-2-carboxylic acid, based on the total weight of organic compounds in the electrochemically reduced product composition. The remainder of the organic compounds preferably consist predominantly (i.e. more than 60 wt %) of furan-2,5-dicarboxylic acid.

[0072] Advantageously the process according to the invention comprises a further step of separating one or more impurity reduction products, such as the one or more reduction products of the 5-formyl-furan-2-carboxylic acid produced by electrochemically reducing such 5-formyl-furan-2-carboxylic acid, from the furan-2,5-dicarboxylic acid. Such further step may comprise acidizing an electrolyte solution comprising the furan-2,5-dicarboxylic acid and the one or more reduction products, thereby allowing the furan-2,5-dicarboxylic acid and optionally one or more reduced products, to precipitate to form a precipitated furan-2,5-dicarboxylic acid composition.

[0073] Such a composition could optionally comprise an essentially colorless furan-2,5-dicarboxylic acid and essentially colorless derivatives of 5-formyl-furan-2-carboxylic acid.

[0074] FIG. 1 illustrates a non-limiting example of the processes according to the invention, wherein a feedstock comprising a furan-2,5-dicarboxylic acid and one or more furan-2,5-dicarboxylic acid precursors (101) is treated in a divided electrochemical cell (103), which divided electrochemical cell (103) comprises a cathode compartment (105) containing a copper mesh cathode (107) and a cathodic electrolyte solution (109), present on both sides of the copper mesh cathode (107), and an anode compartment (111) containing a copper mesh anode (113) and an anodic electrolyte solution (115), present on both sides of the copper mesh anode (113). The cathode (107) and anode (113) are connected to a power supply (117), which power supply provides a suitable potential over the anode and cathode to achieve the oxidation at the anode and the reduction at the cathode. The cathode compartment (105) and anode compartment (111) are separated from each other by means of a semi-porous membrane made from sintered glass (119). In the exemplary process of FIG. 1, the feedstock (101) is introduced into the anode compartment (111) via inlet (121). In the anode compartment (111) the feedstock (101) is contacted with the anode (113) to allow the furan-2,5-dicarboxylic acid precursors to be oxidized into furan-2,5-dicarboxylic acid such as to produce a furan-2,5-dicarboxylic acid composition containing 5-formyl-furan-2-carboxylic acid. The produced furan-2,5-dicarboxylic acid composition (123) is withdrawn from anode compartment (111) via outlet (125) and introduced via inlet (127) into the cathode compartment (105), where the furan-2,5-dicarboxylic acid composition (123) is contacted with the cathode (107) and at least part of the 5-formyl-furan-2-carboxylic acid is electrochemically reduced to produce one or more impurity reduction products, such as 5-hydroxymethyl-furan-2-carboxylic acid. The furan-2,5-dicarboxylic acid and one or more impurity reduction products, such as 5-hydroxymethyl-furan-2-carboxylic acid, (131) are withdrawn from cathode compartment (105) via outlet (129) and forwarded to a crystallization unit to crystallize out a purified colorless furan-2,5-dicarboxylic acid composition (not shown).

EXAMPLES

[0075] The invention is further illustrated by the following non-limiting examples

Example 1 and Comparative Example 1A: Electrochemical Purification of a Crude furan-2,5-dicarboxylic acid Composition in a 0.5M sodium hydroxide Solution

[0076] 50 Milligrams of crude furan-2,5-dicarboxylic acid, 1 milliliter of a 0.5 molar aqueous sodium hydroxide solution (0.5 M NaOH) and a magnetic stirring bar were added to each of the two plastic tubes (Teflon®). The tubes were each closed with a septum. In Example 1, the solution at the bottom of the tube was placed into contact with a nickel foam anode (as the working electrode) and a carbon rod cathode (as the counter electrode). In Comparative Example 1A no electrodes were used.

[0077] In both Example 1 as well as in Comparative Example 1A the magnetic stirring bar was stirred by placing it on a magnetic stirrer. Subsequently both tubes were heated to a temperature inside the reactors of 140° C. In example 1 a current of 0.005 ampere was applied for 1800 seconds. Hereafter both tubes were cooled and a sample was taken from each of the tubes. The content of the samples was determined with gas chromatography and the results are illustrated in Table 1 below. The concentrations of 5-hydroxymethyl-furan-2-carboxylic acid, 5-formyl-furan-2-carboxylic acid, and furan-2,5-dicarboxylic acid are shown in milligrams per millilitre (mg/ml).

[0078] The solution from Comparative Example 1A showed precipitation after a few hours. The solution of Example 1 did not show such precipitation.

Example 2 and Comparative Example 2A: Electrochemical Purification of a Crude furan-2,5-dicarboxylic acid Composition in a 0.5M sodium hydrogen carbonate Solution

[0079] 50 Milligrams of crude furan-2,5-dicarboxylic acid, 1 milliliter of a 0.5 molar aqueous sodium hydrogen carbonate solution (0.5 M NaHCO₃) and a magnetic stirring bar were added to each of the two plastic tubes (Teflon®). The plastic tubes were each closed with a septum. In Example 2, the solution at the bottom of the tube was placed into contact with a nickel foam anode (as the working electrode) and a carbon rod cathode (as the counter electrode). In Comparative Example 2A no electrodes were used.

[0080] In both Example 2 as well as in Comparative Example 2A the magnetic stirring bar was stirred by placing it on a magnetic stirrer. Subsequently both tubes were heated to a temperature inside the reactors of 140° C. In Example 2 a current of 0.005 ampere was applied for 1800 seconds. Hereafter both tubes were cooled and a sample was taken from each of the tubes. The content of the samples was determined with gas chromatography and the results are illustrated in Table 1 below. The concentrations of 5-hydroxymethyl-furan-2-carboxylic acid, 5-formyl-furan-2-carboxylic acid, and furan-2,5-dicarboxylic acid are shown in milligrams per millilitre (mg/ml).

TABLE 1

Example	Conditions	HMFA	FFCA	FDCA**
1A *	no electrodes, 140° C., 0.5M NaOH	0.00	0.06	8.32
1	Ni anode, C cathode, 140° C., 0.5M NaOH	0.04	0.01	9.12

TABLE 1-continued

Example	Conditions	HMFCA	FFCA	FDCA**
2A *	no electrodes, 140° C., 0.5M NaHCO3	0.00	0.05	8.08
2	Ni anode, C cathode, 140° C., 0.5M NaOH	0.03	0.02	8.54

* comparative
**the experiments were calibrated to measure the HMFCA and FFCA concentrations rather than the larger FDCA concentrations.
HMFCA = 5-hydroxymethyl-furan-2-carboxylic acid
FFCA = 5-formyl-furan-2-carboxylic acid
FDCA = furan-2,5-dicarboxylic acid

1. A process for treating a furan-2,5-dicarboxylic acid composition, which process comprises:
introducing a furan-2,5-dicarboxylic acid composition, which furan-2,5-dicarboxylic acid composition contains an impurity compound and which impurity compound is 5-formyl-furan-2-carboxylic acid, into a cathode compartment of an electrochemical cell; and
electrochemically reducing the impurity compound in the cathode compartment.
2. The process according to claim 1, wherein the furan-2,5-dicarboxylic acid is obtained or obtainable, directly or indirectly, by oxidation of a corresponding dialkyl aromatic compound.
3. The process according to claim 1, wherein the cathode compartment contains a cathodic electrolyte solution, which cathodic electrolyte solution has a pH of equal to or below 4.0 or equal to or above 10.0.
4. The process according to claim 1, wherein the cathode compartment contains a cathode containing or consisting of carbon, or containing or consisting of a material chosen from the group consisting of gold, silver, nickel, palladium, platinum, chromium, ruthenium, rhodium, osmium, iridium, indium, bismuth, copper, tin, iron, lead and compounds or alloys thereof and/or hydroxydes and/or oxides thereof.
5. The process according to claim 1, wherein the cathode compartment contains a cathode containing or consisting of a copper or nickel mesh or a carbon cloth.
6. The process according to claim 1, comprising a further step of separating one or more reduction products of the

5-formyl-furan-2-carboxylic acid, produced by electrochemically reducing 5-formyl-furan-2-carboxylic acid, from the furan-2,5-dicarboxylic acid.

7. The process according to claim 6, wherein the further step comprises acidizing the electrolyte solution comprising the furan-2,5-dicarboxylic acid and the one or more reduction products of the 5-formyl-furan-2-carboxylic acid, thereby allowing the furan-2,5-dicarboxylic acid to precipitate to form a precipitated furan-2,5-dicarboxylic acid composition.

8. A process for producing and treating a furan-2,5-dicarboxylic acid composition, wherein the process comprises:

- introducing a feedstock containing a furan-2,5-dicarboxylic acid precursor into an anode compartment of an electrochemical cell;
- electrochemically oxidizing the furan-2,5-dicarboxylic acid precursor in the anode compartment, thereby producing a furan-2,5-dicarboxylic acid composition containing an impurity compound;
- introducing the furan-2,5-dicarboxylic acid composition containing the impurity compound, into a cathode compartment of an electrochemical cell; and
- electrochemically reducing the impurity compound in the cathode compartment, thereby producing one or more impurity reduction products.

9. The process according to 8, wherein the feedstock is a feedstock containing furan-2,5-dicarboxylic acid and a furan-2,5-dicarboxylic acid precursor.

10. The process according to claim 8, wherein the cathode compartment and the anode compartment are part of the same divided electrochemical cell.

11. The process according to claim 8, wherein the cathode compartment is part of a first, divided or undivided, electrochemical cell and the anode compartment is part of a second, divided or undivided, electrochemical cell.

12. The process according to claim 8, wherein the furan-2,5-dicarboxylic acid precursor comprises 5-hydroxymethylfurfural or an ether or ester thereof.

* * * * *